Research Article

Adsorption of anionic dyes monoazo and diazo using organo-bentonites

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Abstract
Adsorption of orange and yellow dyes, containing mono- and di-azoic groups, respectively, were studied by the use of a natural and organo-bentonites, which were obtained by treatment with hexadecyl-trimethyl-ammonium bromide (Br-HDTMA). Two different bentonites from Argentina were used. X-ray diffraction, UV–visible spectrometry, infrared spectrometry and thermal analysis were used for the characterizations. The results were interpreted by using isotherms that fit properly to the mathematical model of Langmuir. The structural and physicochemical properties of the clay, and the arrangement of hexadecyl-trimethyl-ammonium cation ($HDTMA^+$) into the interlayer of the smectites, the main clay mineral composition of the bentonites, were responsible for the retention of dyes. The retention of the azo dyes not only increased with the $HDTMA^+$ modification of the bentonites but also depended on the clay mineral (smectite types) composition of the pristine bentonite.

Keywords Adsorption · $HDTMA^+$ · Organo-bentonite · Azo dyes

1 Introduction

Textile industry is constantly growing and consequently high consumption of dyes also is required. During the staining stage of the fibers, large volumes of various substances are used, among which are the dyes of organic origin [1–3]. The organic dyes contain highly carcinogenic amines and aromatic groups [4, 5], which are not treated properly before being discarded, and being highly soluble in water, they can be transported and reaching the water courses for human consumption. In addition, due to the color they provide to fluvial beds, they impede the natural photosynthetic activity of aquatic plants, preventing the penetration of sunlight, damaging the aquatic biota directly or indirectly [6]. Several scientific publications are focused in studies on the treatment of waste with dye loading by means of physical, chemical, biological and electrochemical treatments; however, none of these methods eliminates the harmful substances, in most cases, only the solutions are decolorized, therefore they are used in combination [4, 5, 7], which requires complex methodologies and higher costs [8, 9]. A solution, economically viable, for this problem is the adsorption using as adsorbent material clays, abundant in nature and with adsorptive properties widely studied, which come mainly from its capacity of cation exchange and large surface area [10]. The retention of dyes in clay minerals will depend both on the physicochemical properties of the dyes, as well as on the adsorbent material. Clay minerals having negative charges between their sheets, and being naturally organophobic, require pretreatment retention tests of anionic organic dyes.

Bentonite is a rock constituted by high smectite clay mineral content with quartz, feldspar, gypsum and/or

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other minerals as impurities. It is known that clay minerals have the natural ability to retain molecules mainly due to the small particle size, the cation exchange capacity and the high surface area. The high hydrophilic character and the positive charge do not allow the retention of the anionic organic molecule; however, to increase the adsorption capacity of this type of molecules, it is necessary to perform an organic treatment in the clay.

The aim of this contribution was to study the retention of anionic azo dyes normally used in the textile industry, by using natural and modified bentonites with $HDTMA^+$. Two azo dyes (Yellow GR and Orange G) with different chemical structure and number of chromophore groups were selected to evaluate the behavior with respect to the natural and organo modified bentonite adsorbent.

2 Materials and methods

2.1 Adsorbents

Two bentonitic-clays from Neuquén and San Juan provinces, Argentina were used in this work. The bentonites were named as Z and S, respectively. Organo-bentonites were prepared by adding hexadecyl-trimethyl-ammonium bromide equal to Cation Exchange Capacity (CEC). An amount of 2 mass% of bentonite in aqueous solutions of HDTMA-Br salt was contacted for 24 h. The solids were washed with distilled water to remove excess salt, separated, and dried at 60 °C. HDTMA-bentonites were crushed to pass a sieve M:200 (< 74 µm) and stabilized at a relative humidity of 55% (RH) before characterization. The samples were named Zo and So.

2.2 Dyes

Yellow GR (Y) and Orange G (O) dyes were selected for adsorption test. The structural formula and main groups content of the dyes are shown in Table 1, both with azoic chromophore (N=N) groups. The concentration of each dye, Yellow GR (Y) and Orange G (O), in water was 125 mg L^{-1}.

2.3 Analysis and characterization

The X-ray diffraction (XRD) of the sample were obtained by using a Philips 3020 Goniometer equipment with PW 3710 Controller, Cu Kα radiation (λ = 1.5405 Å), and Ni filter at 40 kV and 20 mA. The patterns were obtained by scanning at 1° (2θ) min^{-1} between 2.2 and 70° (2θ).

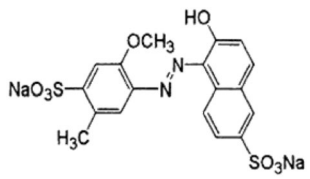
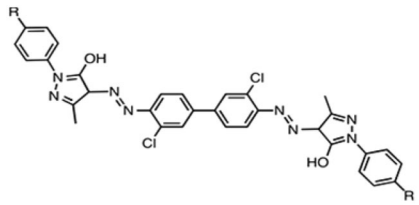
A Netzsch STA 409 analyser at a heating rate of 10 °C min^{-1} and a nitrogen flow rate of 35 mL min^{-1} in a temperature range of 25–1000 °C was used to determine mass loss of the samples.

Fourier transformed infrared spectroscopy (FTIR) spectra using KBr pressed disk technique was conducted on Spectrum One Perkin Elmer equipment. The spectra were collected for each measurement over the spectral range of 400–4000 cm^{-1}.

2.4 Adsorption experiences

Adsorption dye experiments by bentonites (Z and S) and organo-bentonites (Zo and So) were obtained in the range of 400–5000 mg of sample per L^{-1} of dye solution. The dye uptake by solid was calculated from the difference between the quantity of dye added and the quantity

Table 1 Comparison between Yellow GR and Orange G

Orange G		Chromophore	1 Azo 1 Naphthalene	C: 16 N: 2
		Auxochrome	2 Sodium sulfonate	
		Others	1 *p*-Methyl, *p*-methoxy-benzene	
Yellow GR		Chromophore	2 Azo	C: 35 N: 8
		Auxochrome	2-Chlorobenzene	
		Others	2 Hydroxy-pentanamine 2 Benzene	

remaining in the equilibrium solution after 24 h of contact. The amount of retained Y and O dyes was determined by UV–vis, according to what was indicated in various investigations [11–13], measuring of the azo group absorbance (at 400 nm and 485 nm for Y and O dyes solutions) in a Hewlett Packard 8435 spectrophotometer and PG-Instruments Model T60. After adsorption test the samples were named as: Xy-A; where X is the solid: Z, S, Zo or So; y is the amount of solid in mg per mL of dye solution, and A is the dye solution Y or O.

3 Results and discussions

3.1 Characterization of bentonites and organo-bentonites

Z bentonite contains smectite as clay mineral and also feldspar and gypsum as impurities, whereas S bentonite is rich in smectite with a little amount of quartz (Fig. 1).

Figure 2 shows the results of the typical test to identify smectite among other clay minerals (for example kaolinite, illite, etc.). The shifted of 00l reflection peak of the smectite in natural (n) condition, by XRD analysis, to higher and to lower 2° (theta) after calcined at 600 °C (c), and solvated with ethylene glycol (g) conditions, respectively, are characteristics of the smectite clay minerals [14]. Then, the spacing value in natural conditions of the 1.22 nm and 1.40 nm for Z and S samples which were shifted to 1.73–1.72 nm and 0.98–0.97 nm, after ethylene glycol and calcined samples, respectively [15], confirmed the presence of smectite en Z and S bentonites.

There are different types of smectites [14], such as: dioctahedral (montmorillonite, beidellite, nontronite) and trioctahedral (saponite, hectorite, etc.) mainly according to isomorphic substitution in structural composition. Greene-Kelly (GK) test [16] allows differentiate montmorillonite from other dioctahedral and trioctahedral smectites. Figure 3 shows the results of the GK test for S and Z bentonites. The type of smectite in S bentonite is montmorillonite (due to collapsed reflection is present, at 0.93 nm after test), whereas in Z bentonite the addition of the expanded layer at 1.74 nm, nontronite and/or beidellite also can be present.

The intercalations of $HDTMA^+$ in interlayer spacing of the smectite component of each bentonite (Z and S) originated a change from 1.24 to 2.22 nm (So) and 1.19 to 1.91 nm (Zo), Fig. 4. Similar values were reported by Volzone et al. [17], Lee and Kim [18], Zhu et al. [19], Vidal and Volzone [20], and Lagaly [21], after $HDTMA^+$ intercalation to different smectite types, according to different models proposed. The arrangement of an organic cation of long carbon chain, for example $HDTMA^+$ with respect to the sheet of clay mineral, would be located in monolayer when interlayer spacing are between 1.48 and 1.50 nm; in two successive layers (bilayer) when recorded interlayer spacing values between 1.78 and 1.88 nm; pseudotrilayer if *d*(001) values are between 1.89 and 1.94 nm and paraffine arrangement between 1.95 and 2.2 nm. In this work and according the interlayer value of the Zo and So, the organic cation adopted *pseudotrilayer* and *paraffine* arrangements, respectively. These types of arrangements are also related to layer charge of the smectite component [21], where the layer charge of S (0.58) was higher than the component of the Z (0.28). Such values were obtained by calculations of structural formulas [14] of the smectite component corresponding to each bentonite.

Thermogravimetric analysis (TGA) for Z and S bentonites showed a first abrupt mass loss up to 200 °C (10.5% and 17.0% for Z and S, respectively) characteristic of the

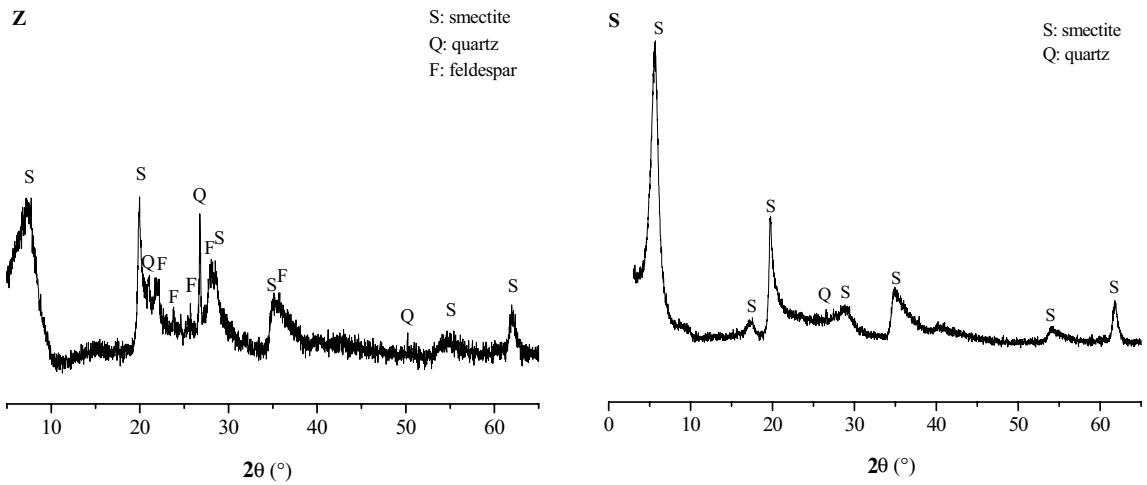


Fig. 1 XRD of Z and S bentonites

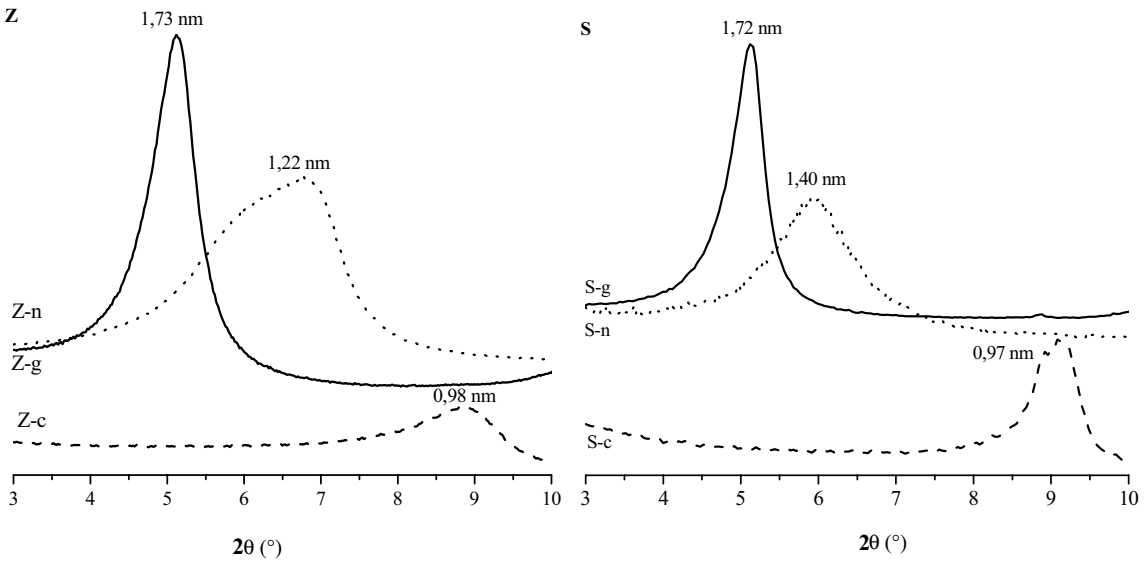


Fig. 2 XRD of bentonites in natural (Z-n, S-n), after solvation with ethylene glycol (Z-g, S-g) and calcined (Z-c, S-c) conditions

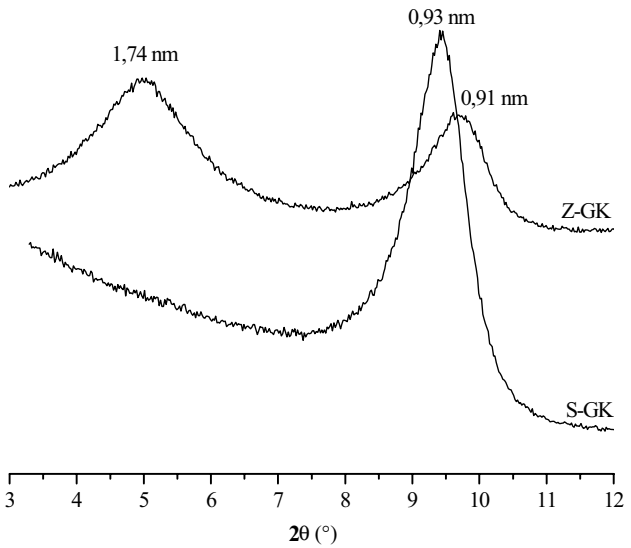


Fig. 3 XRD of Z and S bentonites after Greene-Kelly test

smectite due to water release, either adsorbed on the clay surface or associated to the exchangeable cations in the interlayer spacing (Fig. 5). A second mass loss (5.1% and 4.7% for Z and S) in the temperature range from 500 to 700 °C was attributed to loss of hydroxyl groups of the smectite. The organic intercalation modified such behavior. The mass loss up to 200 °C was reduced drastically to near to 2% and 6% for Zo and So, attributed to change from hydrophilic to hydrophobic character. A higher mass loss occurred continuously with increasing temperature up to 800 °C, assigned also to organic release from the $HDTMA^+$. Finally, the total mass loss of the Zo (22.4%) and So (34.3%) organo-bentonites were higher than natural bentonites Z (15.6%) and S (21.7%).

Analysis by IR spectroscopy (Figs. 6 and 7) allowed to verify that the bands of the Z and S natural clays in the positions of the vibrations of Al–OH (3631–3649 cm^{-1}), H–O–H (3431–3458 cm^{-1}), H–O–H (1630–1670 cm^{-1}); Si–O–Si (1124–1152 cm^{-1}); Si–O–Si (1043–1070 cm^{-1}); Al_2OH (918–941 cm^{-1}), Si–O–Al (522–556 cm^{-1}), typical of montmorillonite-type smectites.

The bands of the Al–Fe^{+3}–OH group (877 cm^{-1}) and Al–Mg–OH group (868 cm^{-1}) in Z and S are attributed to presence of iron and magnesium in higher amount, respectively. The presence of the band at 790 cm^{-1} observed in Z bentonite is due to quartz as an impurity [18]. The quaternary ammonium groups in montmorillonites after treatments (Zo and So) has been confirmed by the bands located at 3022–3056 cm^{-1} (symmetrical stretching of the trimethylammonium head), 2925–2950 cm^{-1} (asymmetric stretching CH in the group $–CH_3$), 2850–2877 cm^{-1} (stretching symmetric CH in the group $–CH_3$) and 1470 cm^{-1} (C–H scissoring in group $C=H_2$) [15–18]. The relative reduction of the bands to 3431–3458 cm^{-1} of the Zo and So regarding to 3631–3649 cm^{-1}, respectively, in agreement with that observed in the thermal tests, is attributable to a change in the hydrophilic surface from clay minerals to hydrophobic, by the replacement of the original inorganic cations between the sheets, by the presence of $HDTMA^+$.

Total organic carbon (TOC) determinated after $HDTMA^+$ treatment indicated a higher content for So (185 mgC g^{-1}) regarding to Zo (157 mgC g^{-1}), which is related to a higher Cation Exchangeable Capacity of the sample (S: 110 meq 100 g^{-1} and Z: 86 meq 100 g^{-1}).

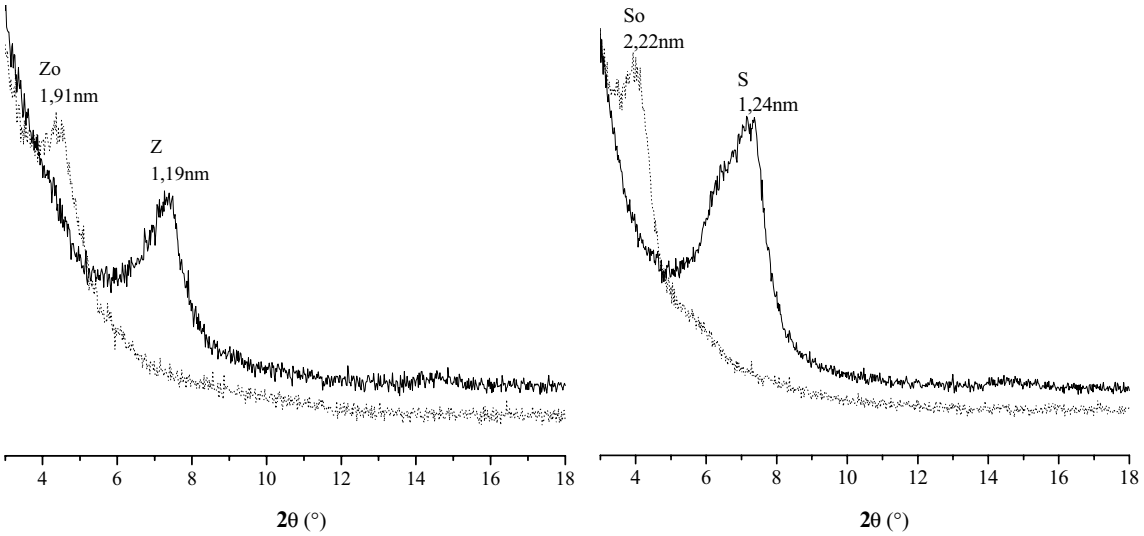


Fig. 4 Interlayer spacing before and after organo-treatment

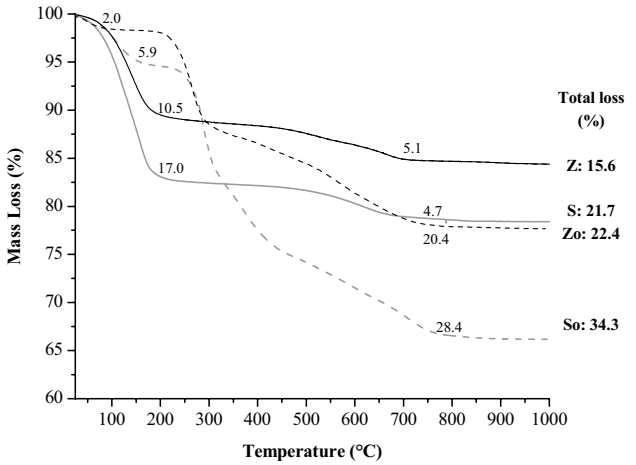


Fig. 5 Analysis thermo-gravimetric of Z, S bentonites and Zo, So organo-bentonites

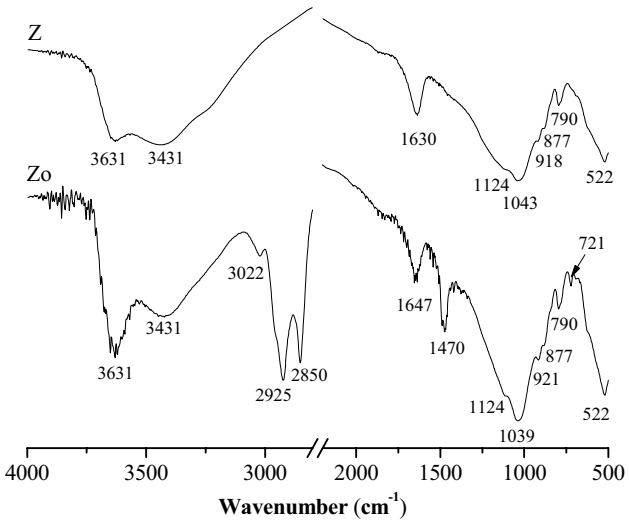


Fig. 6 IR spectra of Z and Zo samples

3.2 Characterization of Yellow GR and Orange G dyes

Y and O dyes showed many bands in IR absorption spectra (Fig. 8). However, absorbance bands of representative groups assigned to Ar–N=N, Ar–N and Ar–Cl at 1456 cm^{-1}, 1243 cm^{-1} and 688 cm^{-1} for Y, and the bands of the groups C_6H_6 (1560 cm^{-1}), N=N (1490 cm^{-1}), C–N (1415 cm^{-1}) and $SO_3^=$ (981 cm^{-1}) to O have been identified.

3.3 Adsorption test

Yelow GR dye aqueous solution (125 mg L^{-1}) showed a broad band centered at 400 nm (azo group) in UV–visible spectra (Fig. 9), whereas the Orange G dye solution showed two bands at 330 nm and 485 nm corresponding to naphthalene and azo groups (Fig. 10), respectively.

Also UV–vis absorption spectra of Y and O dyes before and after retentions by natural and organo bentonites (Z, Zo, Y, and O) are shown in Fig. 9 and Fig. 10, respectively. The addition of different amount of natural bentonites (Z or S) to Y or O solutions (Figs. 9a1, a2; 10a1, a2) were not efficient to remove the dyes because the absorvance of the main bands absorption spectra of the equilibrium concentration were the same of initial concentration. In addition, the UV spectra of the dyes treated with natural bentonite Z (Figs. 9a1 and 10a1) showed an optical effect

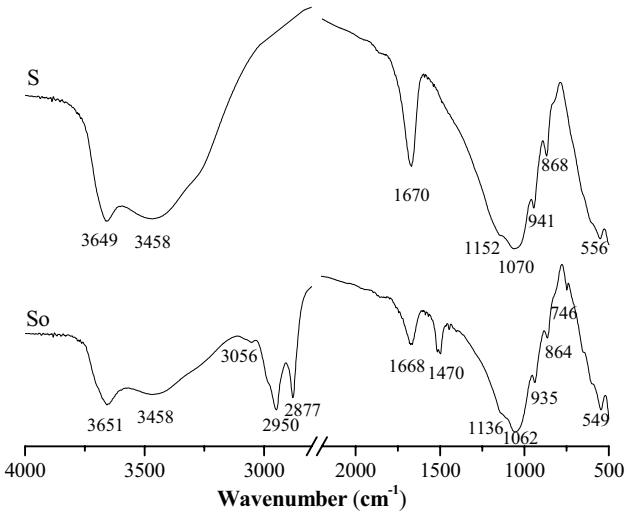


Fig. 7 IR spectra S and So samples

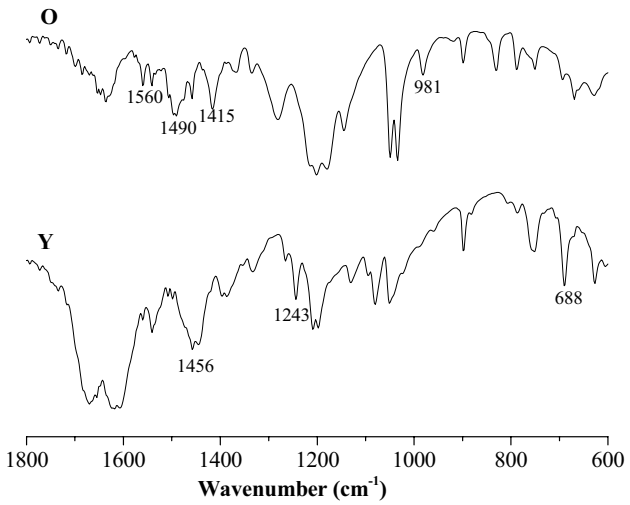


Fig. 8 IR spectra of Y and O azo dyes

of dispersion at approximate wavelengths of 209 nm. This effect was attributed to iron valence states in the lattice of the clay minerals according to studies obtained by Kaickhoff and Bailey [22]. Then, the loss of resolution and the increase in the absorption of sample Z would correspond to the presence of octahedral oxo-Fe(III) oxygen in concordance with IR analysis (Fig. 6, 877 cm^{-1}).

Figures 9a3, a4 and 10a3, a4 shows the spectra of Y and O dyes solutions, respectively, before and after contacted with different amounts of organo bentonites (Zo and So). The absorbance reduction of the dye bands by using a little amount of adsorbents were indicative that the solids can be effective as adsorbents, where Zo was more effective than So.

Adsorption isotherms of the Y and O dyes by organo bentonites are shown in Fig. 11. Generally, the slope decreased as the equilibrium concentration of the dye increase. This type of isotherm is named L according the Giles classification, the first part of isotherm has a high slope, which represents a high affinity at low equilibrium concentrations until the filling of the monolayer, then a decrease in the slope of the isotherm is observed, a consequence of the decrease in the adsorption sites present in the monolayer [23]. The adsorption values of the dye Y with respect to O, by the two orbits is greater for the same equilibrium concentration. Another important difference is that the capacity of retention of Zo is greater than the capacity of So for the same concentration of dye.

Table 2 shows the parameters by applying Langmuir adsorption model. Maximum adsorption of organo-bentonites in their monolayer (Xm) for O and Y dyes equal to 0.113 mmol g^{-1} and 0.277 mmol g^{-1} for Zo were higher than that for So (0.02 mmol g^{-1} and 0.140 mmol g^{-1}). Then, the Zo was better than So as adsorbent and the Y dye was retained in a higher way than O dye.

Zeta potential of natural bentonites and after $HDTMA^+$ intercalation, measured at working pH (5–6) are shown in Table 3. The negative value, − 28 and − 20 mV, of each bentonite (S and Z), justify why the samples cannot retain the anionic dyes used in this paper. The incorporation of organic cation to convert of sample in organo-bentonite originated a very important change in zeta potential, shifting to positive value up to + 10 mV y + 26 mV for So and Zo samples. In this condition the organo-bentonite have the opportunity for retaining the anionic dyes.

3.3.1 Dyes in HDTMA-Bentonites

Table 4 shows the mass loss at 1000 °C of the organo-bentonites (Zo, So) before and after dyes retentions. The total loss in the 31.39–35.19% range of the solid with dyes value were higher than loss of the organo-bentonites 21.70–30.40%, indicating dye retentions. The increase in mass due to dyes, also shown in the table, demonstrated that Zo retained around 10%, whereas So around to 4%.

Figure 12 shows the IR spectra of the organo bentonites after dyes retentions. The presence of the bending Ar–N=N (AZO group) of the Yellow and Orange dyes retaining Zo and So samples appeared at 1490 cm^{-1}, near to the C–H group of the $C=H_2$ at 1469 cm^{-1} (Figs. 6 and 7). The Cl–Ar group band at 686 cm^{-1} of the Yellow dye also was found in Zo and So adsorbents. Unfortunately other bands were not easily seen due to possible overlaps with the bands of the adsorbents.

The used bentonites, Z and S, were mainly constituted by montmorillonite as dioctahedral smectite clay mineral group. However, Z also contained other dioctahedral

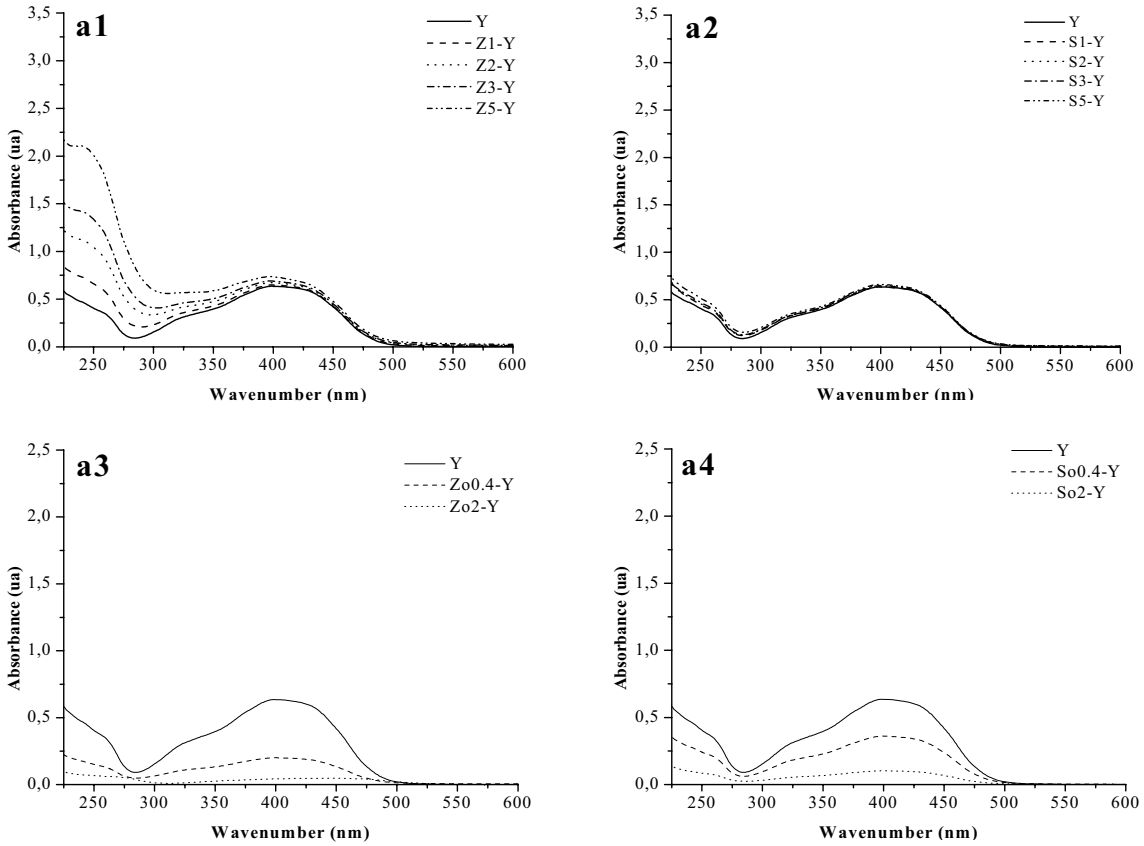


Fig. 9 UV–visible spectra of Y dye solution (125 mg L^{-1}) and equilibrium solutions after different adsorbents. **a1**, **a2** bentonite Z and S at different solid/solution; **a3**, **a4** organo-bentonite Zo and So at different solid/solution ratio

smectite, named beidellite and/or nontronite. The $HDMTA^+$ disposition in interlayer space of the clay mineral in Z and S samples (Zo and So), as pseudotrilayer and paraffine format according to XRD analyses, was attributed to different layer charge of each mineralogical composition and according to Lagaly [21]. The incorporation of $HDTMA^+$ in samples also was corroborated by thermal analysis, detected by an increase in loss mass and by infrared spectra in which characteristic organo bands were found.

The dispersion at 209 nm in UV–visible spectrum of the Z in suspension condition, produced by a colloidal phenomenon, was not observed after organo treatment (Zo). The presence of this type of interference can cause errors in the interpretation of the results, when UV is used for quantifying groups close to the mentioned absorption band.

The presence of only montmorillonite in the S bentonite, and montmorillonite-beidellite/nontronite in the Z as smectitic species, would mark the biggest difference of behavior on the retention of the organic and the studied dyes.

Unmodified clays proved not to be good adsorbents of the studied dyes Yellow GR (di-azoic) and Orange G (mono-azoic), due to their low affinity for organic molecules. However, after the treatment with the organic cation $HDTMA^+$, the organophobic nature of the natural clays varied to organophilic that was proved by the decrease of the physisorbed water, determined by thermal analysis, in the structure of the organo-bentonites. Although both organo-bentonites retained satisfactorily the organic molecules of the Yellow GR and Orange G dyes, in the studied range of the present investigation, the organobentonite Zo showed a greater retention monolayer capacity than So (0.277 mmolY g^{-1} and 0.140 mmolY g^{-1}, respectively, and 0.113 mmolO g^{-1} and 0.020 mmolO g^{-1}).

4 Conclusions

The organic bentonites (Zo and So) obtained by treatment with the $HDTMA^+$ cation were suitable for the retention of the Yellow GR and Orange G dyes, but the pristine bentonites were not recommended.

The dye molecule with the diazo chromophore group (Yellow GR) was retained in an amount greater than that of monoazoic (Orange G) by organo-bentonites.

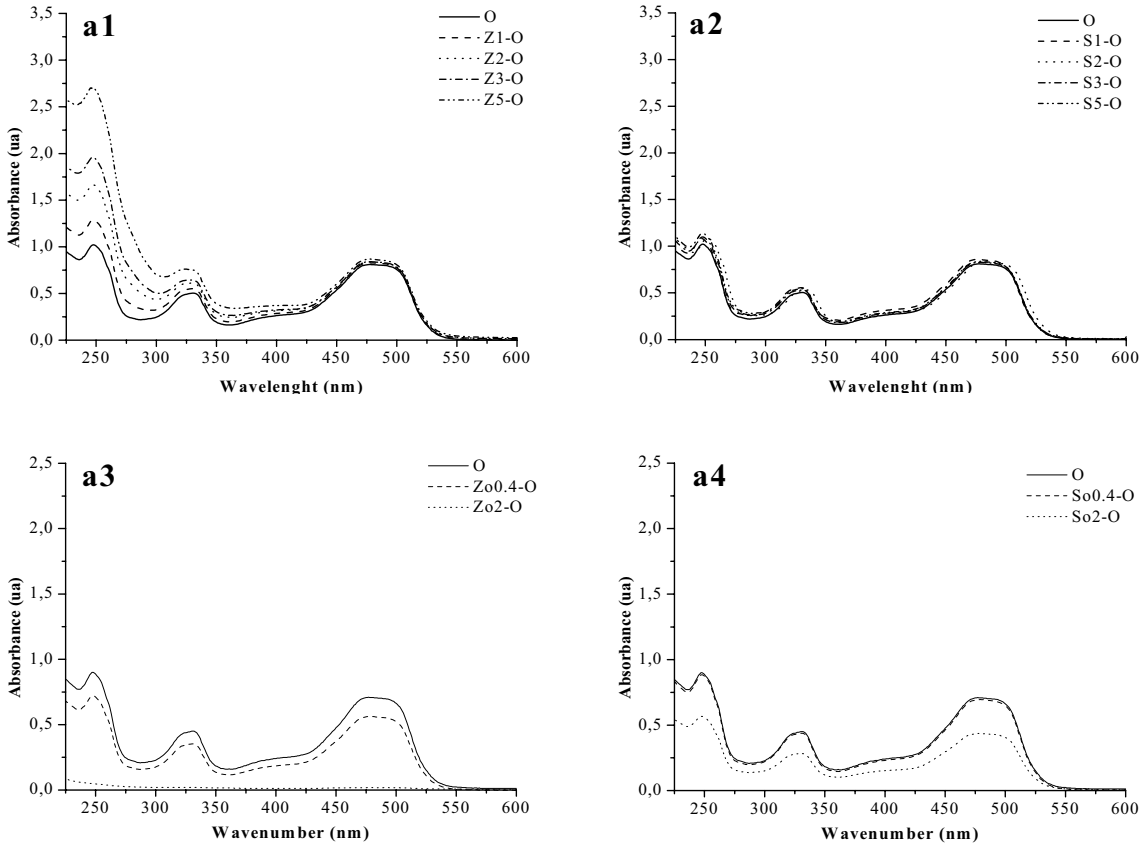


Fig. 10 UV–visible spectra of O dye solution (125 mg L^{-1}) and equilibrium solutions after contact with different adsorbents. **a1**, **a2** Z and S bentonites at different solid/solution ratio; **a3**, **a4** Zo and So organo-bentonites at different solid/solution ratio

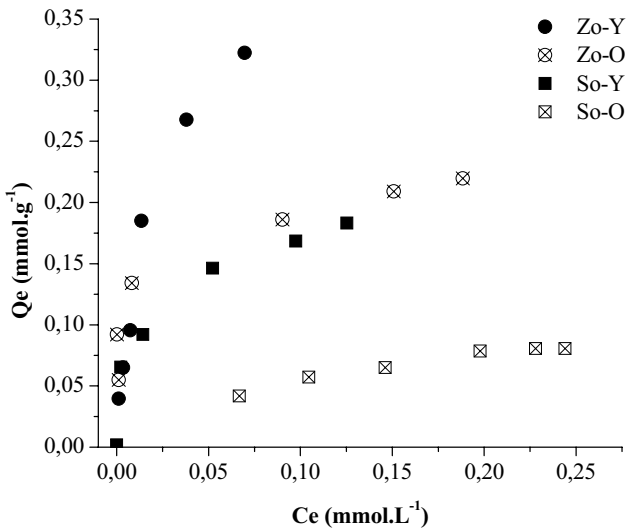


Fig. 11 Adsorption isotherms of Zo and So organo-bentonites for Y and O azo dyes

Table 2 Langmuir parameters for adsorption of Y and O dyes

Samples	Xm (mmol g^{-1})	b (L $mmol^{-1}$)	R^2
So-O	0.020	0.001	0.975
So-Y	0.140	0.046	0.983
Zo-O	0.113	0.028	0.991
Zo-Y	0.277	0.111	0.997

Table 3 Zeta potential of bentonite and organo-bentonite

Adsorbents	Zeta potential (mV)
Z	−20
S	−28
Zo	+26
So	+10

Table 4 Mass Loss up to 1000 °C of Zo and So before and after Y and O dyes retentions

Total mass loss (%)			
Zo-Y	Zo-O	So-Y	So-O
31.39	32.35	35.19	34.04
Zo: 21.70		So: 30.40	
9.69[a]	10.65[a]	4.79[a]	4.00[a]

[a]Difference attributed to dye incorporation

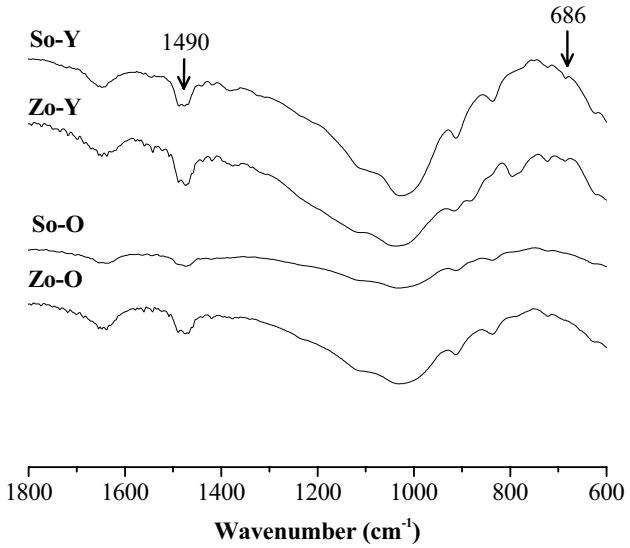


Fig. 12 IR spectra of the organo-bentonites after azo dyes retentions

HDTMA$^+$ was placed in the intermediate layer of smectite clay mineral, the main component of the bentonites. *Pseudo-trilamine* type arrangement of the HDTMA$^+$ cation in the smectite of the Zo produced an increase in the positive density, which was corroborated by the zeta potential values (+ 26), thus providing suitable provisions for the adsorption of the dyes The paraffin type arrangement, acquired by the organ-cation in So, locates the molecules of the organ-cation in almost perpendicular form, whose quantity of positive charges was low (zeta potential + 10) that makes possible a smaller retention of the dyes studied, with respect to Zo.

Synthesized HDTMA-bentonites could be efficient for retaining anion and chromophores azoic type.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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